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Assessing the Methane Emissions from Natural Gas-Fired Power Plants and Oil Refineries

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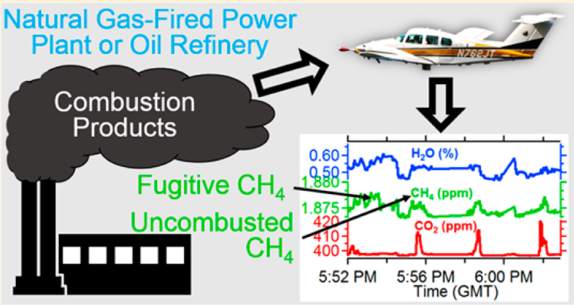
Supporting Information

ABSTRACT: Presently, there is high uncertainty in estimates of methane (CH_4) emissions from natural gas-fired power plants (NGPP) and oil refineries, two major end users of natural gas. Therefore, we measured CH_4 and CO_2 emissions at three NGPPs and three refineries using an aircraft-based mass balance technique. Average CH_4 emission rates (NGPPs: 140 ± 70 kg/h; refineries: 580 ± 220 kg/h, 95% CL) were larger than facility-reported estimates by factors of 21–120 (NGPPs) and 11–90 (refineries). At NGPPs, the percentage of unburned CH_4 emitted from stacks (0.01–0.14%) was much lower than respective facility-scale losses (0.10–0.42%), and CH_4 emissions from both NGPPs and refineries were more strongly correlated with enhanced H_2O concentrations (R^2_{avg} = 0.65) than with CO_2 (R^2_{avg} = 0.21), suggesting noncombustion-related equipment as potential CH_4 sources. Additionally, calculated throughput-based emission factors (EF) derived from the NGPP measurements made in this study were, on average, a factor of 4.4 (stacks) and 42 (facility-scale) larger than industry-used EFs. Subsequently, throughput-based EFs for both the NGPPs and refineries were used to estimate total U.S. emissions from these facility-types. Results indicate that NGPPs and oil refineries may be large sources of CH_4 emissions and could contribute significantly (0.61 ± 0.18 Tg CH_4/yr, 95% CL) to U.S. emissions.



INTRODUCTION

The abundance and accessibility of underground natural gas reserves, paired with rapid technological advancements in horizontal drilling and hydraulic fracturing techniques, have given rise to a booming natural gas industry and record-low natural gas prices. Natural gas is considered a cleaner fuel alternative to coal, producing roughly 56% the amount of CO_2 per unit of energy as coal,[1] and therefore, holds appeal as a "bridge fuel" during transition to renewable energy technologies.[2] Despite the environmental benefits of natural gas as an alternative fuel source, the primary constituent of natural gas is methane (CH_4), a relatively short-lived greenhouse gas with 28–34 and 84–86 times the cumulative radiative forcing of CO_2 on a mass basis over 100 years and 20 years, respectively.[3] Recent studies indicate that CH_4 leakage into the atmosphere may negate its advantages, for instance, a loss rate of 1.5% from natural gas production processes would increase the 20 year climate impact of natural gas by 50%.[4,5] Therefore, identifying significant sources of CH_4 emissions is imperative for effective development of methods to control emissions of greenhouse gases from the oil and natural gas industry.

While CH_4 emission rates from throughout the natural gas supply chain have been recently reported in the literature, there is less understanding regarding emissions from natural gas-fired power plants (NGPP) and crude oil refineries, both of which use large quantities of natural gas[6] and hence are potentially large sources of CH_4 emissions. Increased natural gas consumption by these facility-types has been driven by the combination of low natural gas prices and increased environmental regulations,[7,8] which for instance, has resulted in many coal-fired power plants in the U.S. converting to natural gas for energy generation.[9] Likewise, construction of new NGPPs is also rapidly rising, and in 2015 roughly 40% of new plants producing >1 megawatts (MW) of energy were natural gas-fired.[10] Furthermore, oil refineries are quickly shifting toward natural gas to fuel various equipment-types, including process and utility heaters, hydrogen generation units, and gas turbines, and consumed 893 200 million cubic feet of natural gas in 2014.[11,12]

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Here, we aimed to evaluate emissions from these major natural gas end users by performing a series of measurements of CH_4 and CO_2 emissions at three NGPPs and three oil refineries in Utah, Indiana, and Illinois using an aircraft-based mass balance technique. Hourly CH_4 and CO_2 emission rates are presented and used to obtain CH_4 emission factors (EF) in terms of CO_2 emissions for each facility ($EF_{facility}$). Co-location of CH_4 with CO_2 or H_2O emissions was assessed to understand if CH_4 emissions originated from combustion- or noncombustion-related equipment. Since NGPPs are only required to report combustion-related CH_4 emissions to regulatory agencies,[13,14] we calculated throughput-based CH_4 loss rates and heat input-based EFs for both stack-related combustion emissions as well as total facility emissions and compared our calculated EFs to the Environmental Protection Agency's (EPA) Greenhouse Gas Reporting Program's (GHGRP) default EF.[14] Throughput-based EFs were also calculated for the oil refineries measured in this study. Emissions for both NGPPs and refineries were then extrapolated to the U.S. national-scale using EFs calculated from this data set and U.S. activity factors from the EPA's Air Markets Program Data (AMPD) and Energy Information Administration to estimate total annual emissions from these facility-types. Results from this study support the existing need to better understand the potential of NGPPs and oil refineries as contributors to annual U.S. CH_4 emission totals, while also seeking to elucidate the source of emissions (e.g., combustion- or noncombustion-related) at these facilities.

■ EXPERIMENTAL METHODS

Flight Design and Emission Rate Quantification. Six flights were performed at three combined-cycle NGPPs and three refineries from July 30–October 1, 2015. To quantify facility emissions, an aircraft-based mass balance approach was used and flights were performed using Purdue's Airborne Laboratory for Atmospheric Research (ALAR, https://www.science.purdue.edu/shepson/research/BiosphereAtmosphereInteractions/alar.html), which is a twin-engine Beechcraft Duchess equipped with a Picarro Cavity Ring-Down Spectroscopy (CRDS, model G2401-m) analyzer for real-time, high frequency measurements of CH_4, CO_2, CO, and H_2O.[15−19] The aircraft is also outfitted with a Best Air Turbulence (BAT) probe for high-precision, three-dimensional wind measurements and a global positioning system/inertial navigation system (GPS/INS) for location tracking and wind measurements.[20] Both in-flight and on-ground CH_4 and CO_2 concentration calibrations were performed daily using three NOAA-certified gas cylinders and measurement precisions were ~0.15 ppm (CO_2) and ~1.4 ppb (CH_4).[21]

Prior to each mass-balance flight experiment (MBE), the facilities were circled in-flight to determine if emission of CH_4 or CO_2 was occurring, and if it could be unambiguously attributed to the target. To perform the experiment, a series of 8–14 horizontal transects was flown approximately 1–4 km downwind of the site. Each transect was flown at a unique altitude, ranging from as low to the ground as is safe to the top of the boundary layer and spaced approximately 50–100 m apart. The ends of each transect extended sufficiently past the edge of the plume to measure background air. For MBEs where the top transects do not capture the full height of the plume, a vertical profile was conducted to estimate the height of the boundary layer. The CH_4 emission rate was then calculated according to eq 1 based on previously described methods.[15−19]

$$\text{emission rate}_{CH_4} = \int_0^{z_i} \int_{-x}^{+x} \Delta A \cdot U_\perp \,\mathrm{d}x\mathrm{d}z \tag{1}$$

In eq 1, for each point along the transects, the enhancement of analyte (CH_4 or CO_2) concentration above background concentration, ΔA [mol/m^3], was multiplied by the perpendicular component of the wind speed, $U_\perp$ [m/s]. The resulting point-by-point flux values [mol/m^2-s] across each transect were interpolated to a two-dimensional gridded surface by kriging,[22] integrated laterally across the horizontal width of the plume ($-x$ to $+x$) and vertically from the ground (0) to the top of the boundary layer (z_i), to a resolution of 100 and 10 m, respectively, to provide CH_4 and CO_2 emission rates in [mol/s], which were then converted to [kg/h] to be consistent with industry units. Explanation of uncertainty determination is provided in the SI.

Emission Factor Determination. *Calculation of Facility-Based CH_4:CO_2 EFs ($EF_{facility}$) at NGPPs and Refineries.* U.S. inventories report annual CO_2 emissions for NGPPs and refineries, but currently do not account for CH_4 emissions from noncombustion-related processes. Therefore, a facility-wide CH_4 emission factor based on CO_2 emissions, $EF_{facility}$ [kg CH_4/kg CO_2] was determined for the three NGPPs and three refineries by dividing the mass balance-derived facility-wide CH_4 emission rate [kg/h] by the mass balance-derived facility-wide CO_2 emission rate [kg/h] (eq 2).

$$EF_{facility}\left[\frac{\text{kg } CH_4}{\text{kg } CO_2}\right] = \frac{CH_4\ ER_{facility}[\text{kg } CH_4]}{CO_2\ ER_{facility}[\text{kg } CO_2]} \tag{2}$$

$EF_{facility}$ was then multiplied by annual CO_2 emission rates (kg/h) reported to the GHGRP (for the NGPPs and refineries) and AMPD (for the NGPPs) to approximate annual CH_4 emissions from these facilities. This method assumes that the CH_4:CO_2 ratio is constant throughout the year for simplification. Note that the CH_4:CO_2 ratio was used as an EF due to high accuracy, hourly data for CO_2 emissions from the AMPD.

Calculation of Stack-Based CH_4:CO_2 EFs (EF_{stack}) at NGPPs. For the three NGPPs, emissions were also sampled exclusively from stacks, the primary source of combustion emissions, to derive a stack-based CH_4 emission factor based on CO_2 emissions, EF_{stack} [kg CH_4/kg CO_2]. Stacks were sampled either by flying directly above the stack or by circling the stack at a distance of <200 m. CO_2 peaks were used to determine the start and end points of the stack emission and a linear fit was applied between these points to define background, which was subtracted to give ΔCO_2 and ΔCH_4 (SI Figure S1). A standard linear regression was performed for ΔCH_4 (ppm) versus ΔCO_2 (ppm) using daily stack sampling data from each site and the regressions were forced through zero. The slope of the line (CH_4 ppm/CO_2 ppm) was converted to mass units (e.g., kg/kg) by multiplying by the ratio of the molecular weights of CH_4 to CO_2 (16/44) to yield EF_{stack} [kg CH_4/kg CO_2]. Stack emission factors were also calculated by an alternative method to verify results, as described in the SI. Where available, we compare $EF_{facility}$ to EF_{stack} to better understand the source of facility CH_4 emissions.

Throughput-Based Loss Rates and EFs at NGPPs. To calculate throughput-based loss rates for the NGPPs, hourly CO_2 emission and heat input data for P1–3 was downloaded from the EPA's AMPD Web site (https://ampd.epa.gov/ampd/).[13] Note that heat input is the energy content of fuel given in million British thermal units (mmBtu) where 1 Btu equals 1055 J. Using the start and end times of each flight, the hourly reported data from the AMPD was adjusted based on the true sampling times

Table 1. Facility Emission Rates and CH_4:CO_2 Emission Factors[a]

		CH_4 ER (kg/h)		CO_2 ER (×10,000 kg/h)			CH_4:CO_2 EF (kg CH_4/kg CO_2)		
site	date	MBE (±2σ)	RP	MBE (±2σ)	RP	AMPD hourly	$EF_{facility}$ (EF ± 1σ)	EF_{Stack} (EF ± 1σ)	EF_{stack}/ $EF_{facility}$
P1	9/19	N.U.	2	N.U.	12	12	–	$1.5(\pm0.5) \times 10^{-5}$	–
	9/20	120 ± 90		11 ± 9		12	$1.1(\pm0.6) \times 10^{-3}$	$3.2(\pm0.6) \times 10^{-4}$	0.29
	9/21	75 ± 30		17 ± 6		12	$4.4(\pm1.2) \times 10^{-4}$	$3.3(\pm0.4) \times 10^{-5}$	0.08
	avg.						$7.7(\pm4.4) \times 10^{-4}$	$1.2(\pm0.3) \times 10^{-4}$	0.16
P2	9/19	N.U.	4	N.U.	20	20	–	$7.0(\pm1.5) \times 10^{-5}$	–
	9/20	N.U.		N.U.		20	–	$9.4(\pm2.5) \times 10^{-5}$	–
	9/21	84 ± 76		24 ± 22		23	$3.5(\pm2.3) \times 10^{-4}$	$2.6(\pm1.1) \times 10^{-5}$	0.07
	avg.							$6.3(\pm1.8) \times 10^{-5}$	–
P3	9/25	240 ± 70	2	18 ± 5	10	34	$1.3(\pm0.3) \times 10^{-3}$	$7.8(\pm0.9) \times 10^{-5}$	0.06
R1	7/31	360 ± 200	4	180 ± 110	2.3		$2.0(\pm0.8) \times 10^{-4}$		
	10/1	N.U.		N.U.			–		
R2	7/31	540 ± 210	51	100 ± 60	19		$5.4(\pm1.9) \times 10^{-4}$		
R3	9/25	830 ± 240	27	46 ± 13	28		$1.8(\pm0.4) \times 10^{-3}$		

[a] Abbreviations: ER, emission rate; EF, emission factor; RP, EPA's 2014 Greenhouse Gas Reporting Program data;[14] AMPD, EPA's Air Markets Program Data;[13] fac., facility; N.U., mass balance flight data was not usable due to poor meteorological conditions or due to partial capture of facility emissions.

(see SI). Hourly throughput estimates [kg CH_4/h] were determined using these time-adjusted heat inputs [mmBtu], the conversion factor 1.02 [mmBtu/MCF] (where MCF is 1000 ft^3), the density of CH_4 at 15 °C and 1 atm (19.2 [kg CH_4/MCF]), and the assumption that 95% of natural gas is CH_4, using eq 3.

Using the calculated $EF_{facility}$ and EF_{stack}, projected annual CH_4 emission rates based on annual CO_2 emissions reported to the AMPD and GHGRP were calculated by multiplying EF_{stack} [kg CH_4/kg CO_2] and $EF_{facility}$ [kg CH_4/kg CO_2] by annual CO_2 emissions [kg CO_2/year] and then converting the resulting CH_4 emission rate [kg CH_4/year] to kg CH_4/h.

Annual throughput-based CH_4 loss rates for the NGPPs were then determined (eq 4) for both stack-only emissions and total facility emissions using the calculated projected annual CH_4 emission rates [kg CH_4/h] based on annual CO_2 emissions reported to the AMPD only, since the AMPD is based on real-world measured data from continuous emissions monitoring systems, whereas the GHGRP data is based on engineering calculations using outdated emissions factors.

The EPA's GHGRP currently requires NGPP operators to calculate annual combustion-related CH_4 emissions using a default heat input-based EF of 1.0×10^{-3} kg CH_4/mmBtu. For comparative purposes, a heat input-based EF was calculated based on both stack-only emissions (should be comparable to the GHGRP default EF) and facility-scale emissions from this study (eq 5). Again, the projected annual CH_4 emissions estimates derived from the AMPD CO_2 data was used.

Throughput-Based CH_4 EFs at Refineries. To calculate a throughput-based EF for the three refineries, projected annual CH_4 emission rates based on annual CO_2 emissions reported to the GHGRP were calculated by multiplying $EF_{facility}$ [kg CH_4/kg CO_2] by annual CO_2 emissions [kg CO_2/year] and then converting the resulting CH_4 emission rate [kg CH_4/year] to kg CH_4/h. This hourly emission rate was divided by the hourly throughput [barrels/h] of the specific refinery, determined from 2015 annual throughput data from www.eia.gov, to give a throughput-based EF [kg CH_4/barrel].

$$\text{throughput}\left[\frac{\text{kg CH}_4}{\text{h}}\right] = \text{heat input}[\text{mmBtu}] \times \frac{1\text{MCF}}{1.02\text{mmBtu}} \times \frac{19.2\text{ kg CH}_4}{1\text{MCF}} \times 0.95 \quad (3)$$

$$\text{loss rate}[\%] = \frac{\text{projected annual CH}_4\text{ emissions from AMPD CO}_2\text{ data [kg CH}_4\text{/h]}}{\text{throughput[kg CH}_4\text{/h]}} \quad (4)$$

$$\text{EF}_{\text{throughput-based}}\left[\frac{\text{kg CH}_4}{\text{mmBtu}}\right] = \frac{\text{projected annual CH}_4\text{ emissions from AMPD CO}_2\text{ data [kg CH}_4\text{/h]}}{\text{average hourly heat input [mmBtu/h]}} \quad (5)$$

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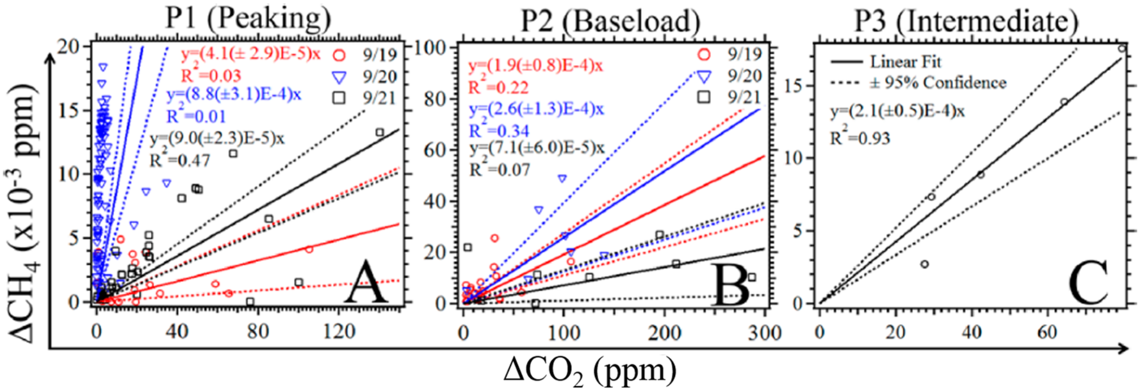

Figure 1. Determination of Stack-Based Emission Factors at the NGPPs for (A) P1 on 9/19, 9/20, and 9/21, (B) P2 on 9/19, 9/20, and 9/21, and (C) P3 on 9/25. Regressions were performed separately for each day of measurement according to the provided figure legends. Solid lines indicate the best fit line and dotted lines represent the 95% confidence bounds.

■ RESULTS AND DISCUSSION

Mass Balance Quantification of Facility CH_4 and CO_2 Emissions. To understand the magnitude of CH_4 emissions from NGPPs and refineries, six flights were performed at three NGPPs and three refineries, resulting in seven usable mass balance flight experiments at the six sites, and stack emission sampling on seven occasions at the three NGPPs (SI Table S1). Meteorological conditions for each flight (SI Table S1) and individual flight paths (SI Figure S2) are provided. The three NGPPs were selected to represent different power plant classifications, (SI Table S2), including peaking (P1), baseload (P2), and intermediate (P3), because the magnitude of emissions from NGPPs may relate to differences in natural gas throughput, and the operational costs of different electric generating units (EGUs) are a driving factor in understanding which power plants are dispatched to satisfy the temporally changing demand for electricity (www.eia.gov). For instance, baseload power plants operate continuously year-round, and generate the required amount, or "baseload", of electricity to match the average load. During periods when energy loads increase, for example, during heat waves or mid-day in summer, peaking facilities are invoked to generate the additional power needed. Alternatively, intermediate or "load-following" plants supplement the power generated by baseload facilities while adjusting their output to correlate with the hourly demand for electricity. Therefore, understanding the differences in emissions from these three power plant classifications will encourage improvements in mitigation strategies as they relate to specific operational conditions. For the peaking facility, P1, we performed mass-balance measurements on Sunday (9/20) and Monday (9/21) during peak hours of electrical demand. Two mass-balance experiments were attempted at the baseload facility, P2 (9/20 and 9/21), however, only the 9/21 experiment was successful due to poor winds on 9/20. Emissions from the intermediate facility, P3, were measured once, during a period of high energy demand.

The three refineries were successfully sampled once each and were selected based on both their proximity to Purdue University and their representation of small- (R1) to large- (R3) scale refineries based on processing capacity (SI Table S3). A second measurement was performed at R1 (10/1), however, interfering emissions from a nearby unknown source prevented determination of an emission rate. Final calculated CH_4 and CO_2 emission rates (kg/h) for each facility are shown in Table 1 to 95% confidence ($\pm 2\sigma$). It is important to note that variable winds during the P1 (9/20) and P2 (9/21) experiments contributed to high uncertainties in the emission estimates.

To increase understanding of the sources and magnitudes of U.S. greenhouse gas emissions, the Environmental Protection Agency (EPA) implemented the Greenhouse Gas Reporting Program (GHGRP) in 2009 with the goal of collecting and organizing self-reported emissions data from NGPPs and refineries emitting greater than 25 000 t of CO_2 equivalent per year (i.e., ~3000 kg CO_2/h, or ~110 kg CH_4/h, etc.). Additionally, the EPA also requires NGPPs to install continuous emissions monitoring systems (CEMS) that measure gas concentrations (e.g., CO_2) continuously from combustion exhaust stacks and report hourly emissions to the Air Markets Program Data (AMPD).[13] For comparative purposes, the 2014 GHGRP annual facility-specific CO_2 and CH_4 emission estimates and the 2015 AMPD[13] CO_2 emissions during the time of our actual measurements are also provided in Table 1. CH_4 emissions data are not available from the AMPD.

For the NGPPs, quantified CO_2 emission rates at P1 and P2 were not statistically different from their emissions reported to the 2014 GHGRP and the AMPD, and calculated CO_2 emissions at P3 were a factor of 1.8 larger than the GHGRP and a factor of 1.9 smaller than the AMPD. However, for all NGPPs, measured CH_4 emission rates were significantly larger than their respective 2014 GHGRP estimates, by factors of 60 (P1, 9/20), 38 (P1, 9/21), 21 (P2), and 120 (P3). Notably, there was a correlation between power plant operating capacity during the time of measurement and CH_4 emission rate (R^2 = 0.85) and CO_2 emission rate (R^2 = 0.65) (SI Figure S3). Significantly larger CH_4 emission rates were also observed at all three refineries when compared to their respective 2014 GHGRP emission estimates, by factors of 90 (R1), 11 (R2), and 31 (R3). Furthermore, measured CO_2 emissions were also larger at all three refineries compared to the 2014 GHGRP, by factors of 78 (R1), 5 (R2), and 2 (R3), although to a lesser extent than for CH_4. Refinery throughput (SI Table S3) was strongly correlated with CO_2 emissions (R^2 = 0.95) and CH_4 emissions (R^2 = 0.73) (SI Figure S3).

Facility-scale CH_4:CO_2 emission factors ($EF_{facility}$) for the NGPPs and refineries, and stack-based CH_4:CO_2 emission factors (EF_{stack}) for the NGPPs were calculated as described and are provided in Table 1. Markedly, in all cases for the NGPPs, the value of EF_{stack} was 6–29% that of $EF_{facility}$, indicating that emissions sampling from only stacks will likely fail to account for the full scale of emissions from a facility. Furthermore, stack

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Table 2. Projected Annual CH_4 Emission Rates using CH_4:CO_2 EF_{fac} and EF_{stack} and Reported CO_2 Emissions to the GHGRP and AMPD

			2014 GHGRP projected CH_4 ER (kg/h) ± 1σ			2015 AMPD projected CH_4 ER (kg/h) ± 1σ	
site	date	2014 GHGRP CO_2[a] ER (kg/h)	$EF_{facility}$-derived	EF_{Stack}-derived	2015 AMPD CO_2[b] ER (kg/h)	$EF_{facility}$-derived	EF_{Stack}-derived
P1	9/19		[c]	2 ± 1		[c]	2 ± 1
	9/20	115 491	130 ± 70	37 ± 7	104 531	110 ± 64	33 ± 6
	9/21		51 ± 13	4 ± 0		46 ± 12	3 ± 0
P2	9/19		[c]	14 ± 3		[c]	14 ± 3
	9/20	196 919	[c]	19 ± 5	199 758	[c]	19 ± 5
	9/21		69 ± 45	5 ± 2		70 ± 46	5 ± 2
P3	9/25	104 613	140 ± 28	8 ± 1	285 001	380 ± 77	22 ± 2
R1	7/31	23 034	5 ± 2	–	–	–	–
R2	7/31	188 628	100 ± 36	–	–	–	–
R3	9/25	282 959	510 ± 110	–	–	–	–

[a]EPA's 2014 Greenhouse Gas Reporting Program (GHGRP) annual facility-specific CO_2 emission rate estimate, [b]EPA's 2015 Annual Air Markets Program Data (AMPD) facility-specific CO_2 emission rate estimate, [c]Sampled stack emissions only

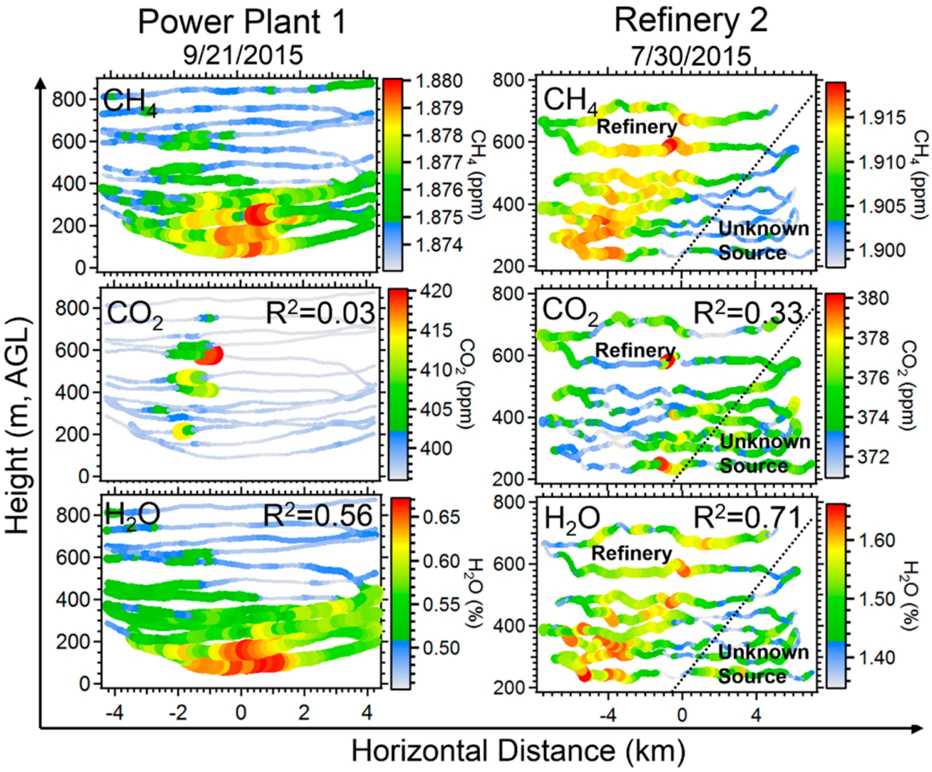

Figure 2. Co-location of CH_4, CO_2, and H_2O Emissions at Power Plants and Refineries. Using Power Plant 1 (P1) and Refinery 2 (R2) as examples, horizontal distributions of raw CH_4 (ppm), CO_2 (ppm), and H_2O (%) concentrations are shown versus height (m, above ground level). Analyte concentration is depicted by color (see color scales) and line width, with warmer colors and thicker line width corresponding to larger analyte concentration. The black dashed lines shown in the Refinery 2 (R2) graphs mark the separation of emissions from different facilities. R^2 values obtained from linear regressions of ΔCO_2:ΔCH_4 and ΔH_2O:ΔCH_4 (SI Figure S5) are displayed in the CO_2 and H_2O concentration panels, respectively.

emissions were sampled three times at both P1 and P2, permitting assessment of temporal variability in the magnitude of EF_{stack}. Regression analysis of total stack plume points for all days of measurement at P1−P3 are shown in Figure 1, organized by day of measurement according to the figure legend. Solid lines represent the best fit and dashed lines represent the 95% confidence bounds, with the slope equaling EF_{stack} (Table 1). At both P1 and P2, daily changes in EF_{stack} did occur by up to a factor of 21 and 4, respectively, despite there being no start-ups or shutdowns of electric generating units between measurements. Stacks at P1 and P2 were sampled at roughly the same time each day (P1: ∼12:00 PM; P2: ∼5:00 PM), on Saturday (9/19), Sunday (9/20) and Monday (9/21). Notably, despite P1 exhibiting the largest EF_{stack} on Sunday 9/20 compared to other measurements, electrical demand was higher during the measurement made on Monday 9/21, according to heat input data reported by the AMPD.

Due to temporal fluctuations in facility emissions caused by variations in facility operations, the hourly emission rates calculated here cannot be directly extrapolated to estimate annual facility emissions. However, this variability can be accounted for indirectly by applying the calculated CH_4:CO_2 EFs to annual CO_2 emissions reported to inventories to estimate a proportional CH_4 emission rate based on the known quantity of

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CO_2 emitted. Therefore, annual average hourly CH_4 emission rates [kg/h] per facility were estimated by multiplying $EF_{facility}$ (NGPPs, refineries) and EF_{stack} (NGPPs) by annual reported CO_2 emission data, first converted from annual to hourly emission rates, from the GHGRP (NGPPs, refineries) and the AMPD (NGPPs), and are shown (±1 σ) in Table 2. These GHGRP-derived hourly CH_4 emission rates can then be extrapolated to estimate the annual atmospheric CH_4 emissions for each facility, which are 800 ± 400 Mg (P1), 600 ± 400 Mg (P2), 1200 ± 200 Mg (P3), 40 ± 20 Mg (R1), 900 ± 300 Mg (R2), and 4500 ± 1000 Mg (R3). Also, for cases at the NGPPs where both EF_{stack} and $EF_{facility}$ were available to estimate annual emissions, $EF_{facility}$-derived emissions were larger than EF_{stack}-derived emissions by factors of 3−22 for both the GHGRP- and AMPD-based projections, again indicating that emissions monitoring methods that only sample stack emissions may significantly underestimate facility emissions.

Assessment of Combustion- and Non-Combustion-Related CH_4 Emissions. To further investigate if CH_4 emissions were related to combustion or noncombustion processes, the correlation of enhanced concentrations of CH_4 with CO_2 and H_2O was assessed along the flight transects. If natural gas undergoes incomplete combustion, uncombusted CH_4 will exist in the presence of combustion products, for example, CO_2 and H_2O. Therefore, CH_4 concentration enhancements along the flight path that are colocated with CO_2 are likely to be uncombusted CH_4 from combustion processes, and at NGPPs, these emissions would originate from exhaust stacks. Alternatively, if CH_4 concentration enhancements are not colocated with CO_2, they likely originate from noncombustion-related equipment on the facility. Figure 2 shows greenhouse gas concentration data along the flight transects for two representative facilities, presented as a horizontal distribution of analyte (CH_4, CO_2, H_2O) concentrations versus altitude. Similar figures for all flights are provided in SI Figure S4. Subsequently, the concentration enhancement above background for all analytes (CH_4, CO_2, H_2O) was calculated along each transect by subtracting an altitude-dependent background and back trajectory analysis was used to spatially segregate emissions from the facility of interest from nearby unknown sources. Linear regressions of these facility-specific concentration enhancements, ΔCO_2:ΔCH_4 and ΔH_2O:ΔCH_4, along the flight paths were then performed, with two representative examples shown in Figure 3 and regressions for all flights provided in SI Figure S5.

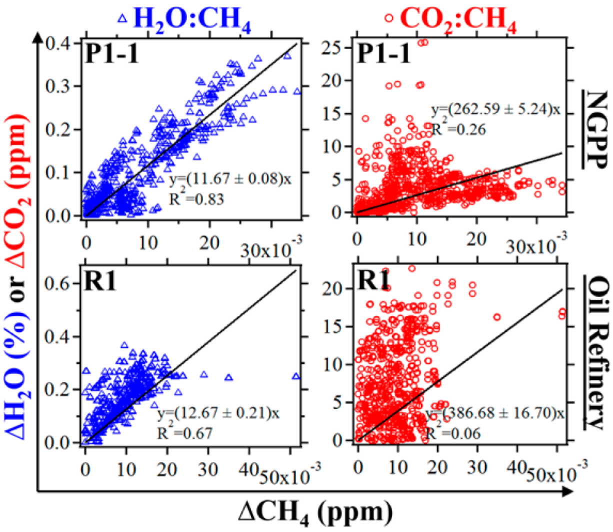

Figure 3. Regression Analysis of H_2O and CO_2 Enhancements versus CH_4 Enhancements Along the Flight Transects. Linear regressions were performed using transect concentration enhancement data from Figure 2 and SI Figure S4, with measurements made at P1 on 9/20 and R1 on 7/31 shown here as examples. Blue triangles (*y*-axis: ΔH_2O; *x*-axis: ΔCH_4) and red circles (*y*-axis: ΔCO_2; *x*-axis: ΔCH_4) show individual data points. Best fit line (black line) with equation and R^2 values are shown. Units of the slopes are [ppm/ppm] for the CO_2:CH_4 curves and [%/ppm] for the H_2O:CH_4 curves.

For all three NGPPs, CH_4 enhancements were more strongly correlated with H_2O enhancements (R^2_{avg} = 0.60), than with CO_2 enhancements (R^2_{avg} = 0.15) downwind of the facilities. The separation of CH_4 emissions from each facility that was observed across the flight path is likely due to variation in the temperature of emissions from different sources within the facilities, which could result in differences in buoyancy of emissions. For instance, if NGPP CH_4 emissions were primarily from high temperature, combustion-related sources (e.g., stacks), then colocation of CH_4 and CO_2 would be expected (this was observed at all three NGPPs in the stack emissions, although to a lesser extent than for colocation of CH_4 and H_2O). Supporting this observation, for all three NGPPs, EF_{stack} was significantly lower than $EF_{facility}$ on all days, further indicating that the majority of NGPP CH_4 emissions are not emitted from stacks. The NGPPs in this study operate on highly efficient combined-cycle systems, which use both natural gas and steam turbines to generate 50−60% more energy than a gas turbine alone by capture and reuse of exhaust heat from the gas turbine into a heat recovery steam generator. Therefore, potential sources of CH_4 emissions at NGPPs include uncombusted CH_4 from stack exhaust (e.g., colocated with CO_2 and H_2O), and fugitive leaks from the facility equipment, including compressors, steam turbines, steam boilers, and condensers (e.g., colocated with H_2O). We can rule out the possibility that our results are caused by dispersion differences of stack-emitted H_2O, CH_4, and CO_2 due to our observation that combustion products (CO_2 and H_2O) and uncombusted CH_4 were colocated at all three NGPPs, with a separate, distinct grouping of CH_4 and H_2O emissions also present, that were not correlated with CO_2. Therefore, it is important to consider nonstack-related emissions at NGPPs when developing facility-scale CH_4 emissions monitoring methods.

The three refineries demonstrated similar results, with CH_4 enhancements being more strongly correlated with H_2O enhancements (R^2_{avg} = 0.71) than with CO_2 enhancements (R^2_{avg} = 0.29), indicating that noncombustion-related CH_4 emissions may be a significant source of total CH_4 emissions at refineries. The equipment involved in petroleum refining, including furnace heaters, hydrogen generation units, gas turbines, and condensers, can be powered by various fuel types, including natural gas. Potentially, refineries may be a source of CH_4 emissions due to increased use of natural gas to power their utilities. Additionally, CH_4 is a minor component of crude oil, and therefore, a product of fractional distillation, and is a product of catalytic cracking. Possible sources of CH_4 and H_2O at refineries therefore include steam boilers, compressor engines, storage vessels, process heaters, process furnaces, and distillation towers. Therefore, inclusion of noncombustion-related CH_4 losses in EF calculations would help encompass a broader range of potential emission sources at these facilities and improve annual emissions estimates in U.S. inventories.

Table 3. Facility Throughput Estimates, NGPP CH_4 Loss Rates, and Throughput-Based EFs

			CH_4 loss rate (%)		throughput-based EF[b]	
site	date	throughput estimate[a]	facility	stack	facility	stack
P1	9/19	41 000	–	0.01 (±0.00)	–	$8.7 (\pm 4.3) \times 10^{-4}$
	9/20	26 000	0.42 (±0.24)	0.13 (±0.02)	$5.0 (\pm 2.9) \times 10^{-2}$	$1.5 (\pm 0.3) \times 10^{-2}$
	9/21	30 000	0.15 (±0.04)	0.01 (±0.00)	$2.0 (\pm 0.6) \times 10^{-2}$	$1.3 (\pm 0.1) \times 10^{-3}$
	avg.		0.29 (±0.14)	0.05 (±0.01)	$3.5 (\pm 1.7) \times 10^{-2}$	$5.7 (\pm 1.6) \times 10^{-3}$
P2	9/19	10 000	–	0.14 (±0.03)	–	$3.7 (\pm 0.8) \times 10^{-3}$
	9/20	56 000	–	0.03 (±0.01)	–	$5.1 (\pm 1.3) \times 10^{-3}$
	9/21	70 000	0.10 (±0.01)	0.01 (±0.00)	$1.6 (\pm 1.1) \times 10^{-2}$	$1.2 (\pm 0.5) \times 10^{-3}$
	avg.			0.06 (±0.02)		$3.3 (\pm 0.9) \times 10^{-3}$
P3	9/25	150 000	0.25 (±0.05)	0.02 (±0.00)	$6.1 (\pm 1.2) \times 10^{-2}$	$3.5 (\pm 0.3) \times 10^{-3}$
R1	7/31	1130	–	–	$4.4 (\pm 1.8) \times 10^{-3}$	–
R2	7/31	8830	–	–	$1.1 (\pm 0.4) \times 10^{-2}$	–
R3	9/25	9940	–	–	$5.1 (\pm 1.1) \times 10^{-2}$	–

[a] P1–3 [kg CH_4/h]; R1–3 [barrels/h]. [b] P1–3 [kg CH_4/mmBtu]; R1–3 [kg CH_4/barrel].

It is estimated that the climate benefit of NGPPs over coal-fired power plants is contingent on total system CH_4 loss rates being less than 3% of throughput, with climate benefits observed immediately.[4] However, life cycle analyses indicate that CH_4 losses that occur from production to distribution and use must also be considered, which are estimated to equal 1.7% of production.[6] In this study, calculated facility-scale loss rates were less than 0.5% in all cases (Table 3), and so the climate benefit of using natural gas for electricity generation is not compromised given the magnitude of losses at the point of use of the NGPPs in this study, if we assume a supply chain leak rate of 1.7% of production. The percentage of unburned CH_4 emitted from stacks at the three NGPPs (0.01–0.14%) was lower than respective facility-scale losses (0.10–0.42%) in all cases, by factors of 3 (P1, 9/20) 15 (P1, 9/21), 10 (P2, 9/21), and 13 (P3, 9/25), again suggesting that more CH_4 is lost from non-combustion-related equipment than from combustion processes (Table 3). Furthermore, the observation that the majority of NGPP and refinery emissions are from noncombustion-related equipment would support the significant discrepancies between our calculated CH_4 emission rates and those reported to the 2014 GHGRP, which only requires reporting of combustion-related CH_4 emissions. The 2014 GHGRP CH_4 emission rates reported for the three NGPPs were all <4 kg/h.

In 2014, the GHGRP required power plants to calculate and report emissions related to general stationary fuel combustion (GHGRP, subpart C) and electricity generation (subpart D), and combustion-related CH_4 emissions were calculated by operators using a required heat input-based emission factor (EF_{GHGRP}) of 1.0×10^{-3} kg CH_4/mmBtu.[23] To examine the accuracy of EF_{GHGRP}, we used our measured data to derive EF_{stack} [kg/mmBtu] for the NGPP stacks (P1, $N = 3$ days of measurements; P2, $N = 3$; P3, $N = 1$) and $EF_{facility}$ [kg/mmBtu] for the complete facilities (P1, $N = 2$ days of measurements; P2, $N = 1$; P3, $N = 1$) (Table 3). For all measurement days, all three NGPPs' EF_{stack} [kg/mmBtu] values were larger than EF_{GHGRP} by an average factor of 4.4, ranging from 0.9 to 15 times larger. More notably, however, is the difference between the complete facility-derived $EF_{facility}$ [kg/mmBtu] and EF_{GHGRP}, which were factors of 50 (P1, 9/20), 20 (P1, 9/21), 16 (P2), and 61 (P3) times larger than the industry-used EF_{GHGRP}. Therefore, updating heat input-based CH_4 EFs at NGPPs may improve the accuracy of GHGRP data, which policymakers rely on to best understand U.S. CH_4 emission rates and the contributions of individual sources.

In addition to reporting general stationary fuel combustion-related emissions (GHGRP, subpart C), refineries are also required to report CH_4 emissions from asphalt blowing operations, uncontrolled blowdown systems, catalytic cracking and reforming units, delayed coking units, flares, process vents, storage tanks, and equipment leaks (subpart Y).[23] Similar to subpart C, emission estimates reported under subpart Y also are calculated using default EFs which may be outdated and could cause inaccurate estimation of annual emissions. Additionally, emissions may also originate from other types of process equipment, including boilers, process heaters, furnaces, incinerators, and thermal oxidizers. Our results suggest that both CH_4 and CO_2 emissions may be underestimated for these three refineries by the GHGRP. To determine if these results are representative of the full range of operating conditions will require further observations.

NGPPs and Refineries as Contributors to U.S. CH_4 Emissions. We estimate that NGPPs in the U.S. emit 0.46 ± 0.17 Tg CH_4 annually (SI Table S4) by using the average of the heat input-based EFs calculated from this study for the NGPPs [kg CH_4/mmBtu] and annual total heat-inputs for all NGPPs nationwide in 2015 as the activity factor (downloaded from the AMPD). Additionally, using the average of the throughput-based EFs calculated from this study for the refineries [kg CH_4/barrel] and the hourly throughput for all refineries in the U.S. in 2015 based on data from www.eia.gov [barrels/h], we estimate that U.S. refineries emit 0.15 ± 0.05 Tg CH_4 annually (SI Table S4). Combined, NGPPs and refineries are therefore estimated to contribute ~0.61 Tg CH_4 annually to U.S. emissions. By comparison, the EPA estimated that oil and gas operations emitted 9.8 Tg CH_4 in 2014, of which CH_4 emissions from NGPPs (0.01 Tg CH_4) and refineries (0.02 Tg CH_4) were estimated to be negligible by comparison.[6] For comparison, U.S. landfill operations and enteric fermentation processes were estimated to emit 5.9 and 6.6 Tg CH_4, respectively, in 2014. Therefore, consideration of improved emissions monitoring and reporting procedures for NGPPs and refineries would significantly improve U.S. inventory emissions estimates. Note that this is a preliminary estimate and that additional sampling is needed to improve robustness of the estimate. However, total emissions from NGPPs is likely to increase in the future as our reliance on NGPPs increases.

Results from this study indicate that NGPPs and crude oil refineries may be significant contributors to annual CH_4 emissions in the U.S., despite lack of facility emission reporting

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in U.S. inventories. Furthermore, results suggest that the primary source of CH_4 emissions at these facilities may be from noncombustion sources, partially explaining why inventory estimates appear biased low as EFs only consider combustion-related emissions. Future studies should aim to identify the specific emission sources at a larger sampling of these facilities, potentially by use of infrared cameras, and subsequently recalculate more robust EFs that consider these sources. Knowledge of common equipment sources would also help inform improvements in emissions mitigation strategies at these facilities, for example, by replacement of aging and faulty equipment, installation of carbon capture devices, and upgrades to improved control technologies related to the specific emission sources. Furthermore, updating CEMS to include hourly CH_4 emission monitoring would help account for combustion-related CH_4 emissions, which were also underestimated in this study.

While measurements in this study were performed during peak operating hours, emissions during periods of start-up and shut-down may be different. Therefore, future measurements at both NGPPs and refineries should be conducted during the full range of operations to develop more robust EFs for each operating condition. Top-down approaches, such as the aircraft-based mass balance technique described in this study, offer the ability to measure total facility emissions to calculate more comprehensive EFs that account for CH_4 emissions from both combustion- and noncombustion-related processes.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.est.6b05531.

Four tables and six figures (PDF)

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Notes

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■ ABBREVIATIONS

ALAR	Airborne Laboratory for Atmospheric Research
AMPD	Air Markets Program Data
CH_4	methane
CO_2	carbon dioxide
CRDS	cavity ring-down spectrometer
EF	emission factor
EPA	Environmental Protection Agency
GHGRP	GreenHouse Gas Reporting Program
LT	local time
mmBtu	million British thermal units
NGPP	natural gas-fired power plants
NOAA	National Oceanic and Atmospheric Administration
SI	supporting information

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■ NOTE ADDED AFTER ASAP PUBLICATION

The throughputs for refinery R1 and R3 were inadvertently switched, and this affected the downstream calculated values in the version of this paper published March 6, 2017. The values were corrected in the article and Table S4 of the Supporting Information and reposted on March 10, 2017.